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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

THE CONTACT-POTENTIAL BETWEEN METALS AND
FUSED SALTS, AND THE DISSOCIATION OF FUSED
SALTS.

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Received October 10, 1898.

Presented by Theodore W. Richards, October 12, 1898.

THE potential difference between fused salts and metals immersed in them is a quantity of great importance because of its relation to the theory of the origin of contact-potentials, on account of the light it throws upon the degree of dissociation of salts in their fused state, and in view of its bearing upon the electrolytic separation of the metals. Notwithstanding these important relations, the subject has received practically no attention at the hands of scientific investigators. In a few cases cells containing fused salts as the electrolyte have been measured, but always with some other end in view than the study of the single potential difference between metal and salt.*

The practical difficulties in the way of carrying out an exhaustive investigation of this subject are many. Among the more important of these are the fact that many salts decompose below or slightly above their melting point, the disturbing effect of side reactions which at ordinary temperatures would be so slow as to cause little or no inconvenience, and the impossibility of using glass vessels at temperatures as high as the melting points of most inorganic salts. Such difficulties as these have prevented me from extending the investigation rapidly, but the results

* Lash Miller (*Zeit. für phys. Chemie*, X. 459, 1892) used fused salts in experiments to prove that there was no change in the contact-potential as the metal changed from liquid to solid state.

Poincaré (*Ann. chim. et phys.*, [6.], XXI. 289, 1890) measured reversible cells containing melted zinc and tin salts with the heat of reaction as the end in view. He investigated also some polarization phenomena with silver electrodes.

from the cells so far measured seem of such value that I give them in this preliminary paper, hoping to extend the investigation to other salts and metals in the near future.

For dilute water solutions the variation of the potential between a metal and a solution of a salt, whose kation is the metal of the electrode, is given by the well known Nernst formula,*

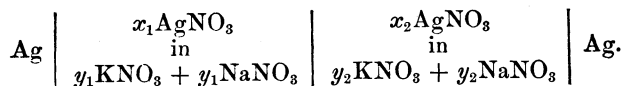
$$E_1 - E_2 = \frac{RT}{n} \log_e \frac{C_2}{C_1},$$

where E_1 , E_2 , are the respective potentials for the concentrations C_1 , C_2 ; R , the gas constant; T , the absolute temperature; and n , the valency of the metal. In the derivation of this formula the gas law, $p v = RT$, is applied to the dissolved salt, and complete dissociation is assumed. In case the dissociation is not complete, C_1 , C_2 , denote the concentration of the dissociated part.

For fused salts, in case the solutions are sufficiently dilute, we might expect the same or an analogous formula to hold. Any experimental evidence, however, for the applicability of the gas law to fused salt solutions, or as to the amount of dissociation, has been lacking.

Accordingly, the first question to be determined was whether or not, for any measureable range of concentrations, the potential difference would vary according to the Nernst formula.

So far all my observations have been upon silver electrodes immersed in fused mixtures containing varying amounts of silver salts. Most of the cells measured were simple silver nitrate concentration cells of the type,



The mixture of potassium and sodium nitrates, rather than either alone, was used as solvent in order to obtain a lower melting point.

EXPERIMENTAL.

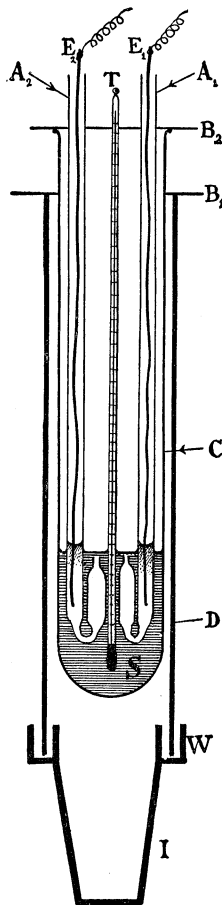
General. — In a few preliminary measurements I tried keeping the temperature constant with an air bath, but was unable to attain much constancy, and therefore substituted a vapor bath. The practical arrangement of the cell in its constant temperature vapor bath is shown in the opposite figure.

* See Nernst, Zeit. für phys. Chemie, IV. 129, 1889.

The jacket *D*, containing the vapor, is a thin-walled glass cylinder about 5 cm. in diameter, joined below by means of a Wood's metal or mercury joint, *W*, to a cast-iron cup, *I*, on which the heating flame plays. This vapor bath arrangement is such as is in common use for V. Meyer vapor density determinations at moderately high temperatures, except that in the present case the jacket tube was shortened. Inside of this vapor jacket is the large test tube *C*, extending about 25 cm. below the top of the outside jacket. So much of the upper opening of the cylinder *D* as the tube *C* does not fill is closed with the asbestos sheet *B*₁. This covering is of course not air tight, but makes it possible for the vapor to ascend near the top without any rapid escape into the room. In the tube *C* is the cell to be measured. It consists of the silver electrodes *E*₁, *E*₂, in the tubes *A*₁, *A*₂, which contain the two differently concentrated solutions of silver nitrate, and the connecting solution *S*. The capillary ends of the tubes *A*₁, *A*₂, were lowered beneath the surface of the connecting liquid only long enough for the measurements to be taken. In order to prevent air circulation, the top of the tube *C* was covered with an asbestos sheet having holes for the tubes *A* and the thermometer *T*.

The heat was supplied by a three-tube Bunsen burner, fed from a gas supply containing a good pressure regulator. By reason of this regulator, when the gas was once adjusted, no care was required to keep the height of the vapor constant, except as the amount of boiling substance made slow escape into the room. The top of the condensing vapor column could be plainly seen, and was kept constant about 18 cm. above the lower end of the tube *C*. With this arrangement any difference in temperature between the upper and lower part of the liquid *S* was unnoticeable.

Temperature. — The cells were measured at two temperatures, that of boiling diphenylamine, and of boiling chinoline. The former was taken



One Fourth Natural Size.

from the laboratory stock, and the latter was made for me by Mr. J. B. Churchill, whom I wish to thank for providing me with a very considerable amount. Since the temperatures were read on a mercury thermometer in the cell itself, no attempt was made to attain absolute purity in the boiling substances.

The most of the cells measured were liable to variations due to other causes than change of temperature of about 0.001 volt. This was the accuracy of measurement aimed at. As it was found to require a change of about 5° in temperature to cause a change of 0.001 volt, the temperatures were read on a thermometer graduated to degrees, and considered constant as long as they did not vary more than 1° .

In order to standardize the thermometer used, it was tested with pure naphthalene. According to Crafts,* naphthalene boils under 756 mm. pressure at $217^{\circ}.9$. The thermometer used for these experiments registered 218° as the boiling point under the same pressure. The actual readings of the thermometer were therefore taken as correct.†

Change in Concentration.—In order to render the danger of change in concentration in the neighborhood of the electrodes as small as possible, the tubes *A* were given the shape shown in the figure. In the preliminary measurements, however, there was still trouble on this account. This was due to the fact that the salts were put into the tubes in the unmelted state. Air was unavoidably retained when the salt was fused, which must necessarily be blown out after the tubes were lowered under the level of the connecting solution, and the latter was thus brought into the tubes. As the potentials were measured by means of a capillary electrometer, even when the air filled the whole cross-section of the capillary, the measurement could be made; the value was, however, always different from the true one. In order to avoid this trouble due to air bubbles, the filling of the cell tubes with the pulverized salts was

* Amer. Chem. Journ., V. 307, 1883-84.

† Graebe (Annalen [Liebig's], CCXXXVIII. 362) finds the boiling point of diphenylamine to be 302° . The earlier determinations of Hofmann, Girard and Wilson, and Kreis, etc., are evidently incorrect, as Graebe standardized his thermometers with benzophenone, according to the figures of Crafts. Whether the difference between Graebe's 302° and the reading 298° of my thermometer in the cell surrounded by the diphenylamine was due to impurities in the latter, to a change in the value of the marked degree between 218° (the point found to be correct), or to the fact that the thermometer in the cell was at a little lower temperature than the surrounding vapor, I have not attempted to determine, since a change of even 4° in temperature would cause a change in voltage in the cells measured of less than 0.001 volt.

abandoned. Instead, the salts were first melted in a test tube, and when they were about the temperature of the constant temperature bath, the cell tubes were filled by immersion, and then transferred to the tube *C*. After this method of filling was adopted, no change of concentration was noticed.

The Connecting Solution.—The solution *S*, which served to connect the two differently concentrated silver nitrate solutions, consisted of equal parts potassium and sodium nitrates, with some silver nitrate. For the cells of small concentration it contained the same proportion of silver nitrate as the less concentrated of the solutions in the tubes *A*. Since it was found experimentally that the amount of silver nitrate in this connecting solution had no effect on the value of the potential, for the concentrated cells it was not accurately determined, but was about 10% AgNO_3 .

Preparation of Solutions.—The potassium and sodium nitrates used were purified by recrystallization. Crystallized argentic nitrate is easily obtained in a condition pure enough for the end in view.

The concentrations of the silver nitrate ranged from 0.001 of total weight to pure silver nitrate. 50% and 10% solutions were weighed out and fused in rather large quantities, and the other solutions made by dilution of these.

The Molecular Concentrations.—While the solutions were naturally made up by weight, it is the molecular volume concentrations, which are to be used in the calculation. In order to obtain these it was necessary to measure the specific gravities of the several mixtures. This was done at the temperature of the chinoline bath, 236°. Since the expansion coefficients for these salts, as found by Poincaré,* are small, we can for our purpose consider the concentrations at 298° to be the same. In order to obtain the specific gravities, tubes of about 0.5 cm. internal diameter were narrowed still more a few centimeters from the lower closed end, and filled to a marked point on the narrow portion of the tubes while in the chinoline bath. After cooling, the tubes were broken off at the marked point, weighed, and the volumes determined by weighing with water, applying the correction for expansion of the glass. The specific gravities measured, and the molecular concentration calculated therefrom are given in the following table.

* *Loc. cit.*

TABLE I.

Per Cent by weight AgNO_3 .	Specific Gravity.	g.-mol. AgNO_3 in liter.
0.1	1.84	0.0108
1.	. . .	0.11 (estimated).
10.	2.02	1.16
50.	2.61	7.68
100.	3.82	22.5

The Electrodes. — Pure silver wires served as electrodes. It was found experimentally that no special care need be taken as to the character of their surface. In view of the irregularities shown by solid metal electrodes in water solutions, this independence of the character of the surface and previous treatment of the electrodes is quite remarkable. As a matter of precaution the wires were scraped with a clean knife, washed, and dried with filter paper before using. Tests were made on several electrodes so treated by putting them into the same solution. They did not give a difference of potential of more than 0.0001 volt.

Measurement of the Potential Difference. — Above the cell tubes the silver wires were soldered to copper ones, and the potential difference measured by the Poggendorf method, using a Leclanché cell, an Ostwald potential box, and a capillary electrometer. A previously standardized one-volt Helmholtz cell was taken as the standard of electromotive force. The electrometer was read with a microscope, and would readily show a difference of 0.0004 volt.

No noticeable error could result from the possible difference in temperature of the two copper-silver junctions.

The Conductivity of Glass. — Although the temperatures used for these nitrate cells were far below the softening point of glass, its conductivity is, even at 200° , very considerable, being of about the same order of magnitude as a $\frac{1}{100000}$ normal KCl solution. Measurements could indeed be made with the capillary electrometer without having any liquid connection between the two AgNO_3 solutions. The potentials so measured (with the two cell tubes closed at the lower end) differed from the true ones generally by about 0.02 volt. The conductivity, however, of the fused salts is so great as to preclude any disturbance from conductivity of the glass when the liquid connection is made.

RESULTS OF THE EXPERIMENTS.

The potentials of four such silver nitrate cells are given in the following table. The calculated values are obtained by substitution of the absolute temperatures and the molecular concentrations, as given in Table I., in the Nernst formula,

$$E_1 - E_2 = RT \log_e \frac{C_2}{C_1}.$$

TABLE II.

SILVER NITRATE CELLS.

No.	Per Cent AgNO ₃ .		Chinoline bath.			Diphenylamine bath.		
	Sol. 1.	Sol. 2.	T.	E. M. F.		T.	E. M. F.	
				Calc.	Observed.		Calc.	Observed.
1	1.	0.1	232	0.101	0.100	298	0.114	0.110
2	10.	1.	"	0.102	0.100	"	0.115	0.112
3	50.	10.	236	0.082	0.071	"	0.093	0.080
4	100.	50.	"	0.045	0.039	"	0.051	0.045

In general I can say that the measurements were all repeated several times, and only in a few cases were there single measurements varying as much as 0.001 of a volt from the mean as here given. The behavior of the several cells with regard to their constancy requires individual mention.

No. 1, at 298°, decreased rapidly in potential after first setting up, but when the 0.1% solution was replaced by that of the outside connecting solution (of same concentration), the value 0.110 volt was always obtained. Five minutes later it had always decreased, in one case to as low as 0.100 volt. This rapid decrease in value may account for the fact that the observed value is 0.004 volt less than the calculated. Had the measurement been taken *immediately* after the fresh solution came in contact with the electrode, the observed value might have been larger. This value was obtained repeatedly, however, the measurement being taken about one minute after the introduction of the fresh solution into the cell tube.

In the chinoline bath cell No. 1 remained constant for from ten to fifteen minutes, and then decreased. It could be brought back to the

original value by replacing the weaker of the two solutions with that of the connecting solution (of the same concentration).

Cell No. 2, at 298° , remained constant for at least twenty minutes after the 1% solution in the neighborhood of the electrode was replenished. Of four cells measured, one decreased in value, and three increased, on standing.

This cell in the chinoline bath remained constant for several hours.

Cells 3 and 4 were extremely constant for several hours at a time, and the same solutions in the same tubes could be heated up several days in succession, and would always give the same value.

The inconstancy of the cells containing very dilute solutions would seem to indicate that in these there is a slow reaction going on between the solution and the electrode. The fact that the replenishing of the solution with that which had not been in contact with the electrode always brought the cell back to the same value, shows that the reaction did not take place throughout the solution as a whole, but only in the neighborhood of the electrode. The more rapid variation at the higher temperature shows that, whatever the reaction may be, its speed increases with the temperature. Obviously a slow dissolving of the silver electrode in the fused salt would account for the observations, the weak solutions being much more affected by this possible irregularity than the strong ones; but this hypothesis is not advanced as a certainty.

The observed values for the cells No. 1 and No. 2 agree remarkably well with the calculated. We must conclude that the osmotic theory of electromotive forces can be extended to the case of fused salts, and that even in a 10% solution the silver nitrate is almost wholly dissociated.

In considering the observed potential to be the difference between the two electrode potentials, we assume that the potential difference between the two differently concentrated solutions is so small as to be negligible. While the good agreement between the values found and calculated is the strongest argument in favor of this supposition, it is to be inferred also from what we know of aqueous solutions. Such potential differences depend on the difference in transference numbers of the two ions. Nernst and Loeb,* and more especially W. Bein,† have shown that the transference numbers all tend toward the value 0.5 as the temperature increases. For AgNO_3 especially, they are never far from 0.5, and approach very near it at the highest temperature measured. W. Bein

* Zeit. für phys. Chemie, II. 962, 1888.

† Wied. Ann., XLVI. 69, 1892.

found for the transference number of NO_3 in AgNO_3 , 0.470 at 20° , and 0.490 at 90° .

Dissociation. — In view of the agreement with the formula in case of dilute solutions, the consideration of the cells containing the more concentrated solution becomes of greatest interest. It seems probable that the deviations from the calculated values are here due entirely to incomplete dissociation. We thus have a means of calculating the degree of dissociation for the 50% AgNO_3 solution, and for the pure salt. The results of this reckoning are given in Table III.

TABLE III.

DISSOCIATION OF SILVER NITRATE.

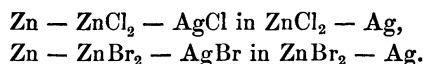
Temperature 236° . Dissociation 0.1% sol. assumed complete.

Per Cent AgNO_3 .	$\text{Log } \frac{C_2}{C_1}$		Degree of Dissociation.
	By Measurement.	Calc. from E. M. F.	
50.	2.8508	2.6912	0.69
100.	3.3172	3.0784	0.58

This is, so far as I know, the first determination of the degree of dissociation of a fused salt. To say that pure fused silver nitrate is 58% dissociated seems at first thought somewhat incredible; especially when we think of the almost infinitesimal dissociation of water and other liquids at ordinary temperatures. These are not the only measurements, however, that go to show that the degree of dissociation is large. Their large conductivities, and the small range of the same when different salts are considered, are in favor of it. The careful measurements of Poincaré* on the conductivity of fused salt mixtures show a behavior very different from that of electrolytic solutions at ordinary temperatures. In the latter case the conductivity is generally greatly changed, or first made possible, by the mixing, while for fused salts the conductivity is almost an additive property of the separate salts. The large amount of dissociation gives at least a qualitative explanation of this apparently anomalous behavior.

* *Loc. cit.*

Before the above cells were measured, cells of the following types were studied:—



The observed values corresponded roughly with those calculated, but the readings were not constant enough to be worthy of detailed mention. In the hope of securing greater constancy silver was substituted for zinc, and two different strengths of argentic halide dissolved in zincic halide were used around the electrodes, as in the experiments with the nitrates. These also were not constant, and some interesting phenomena concerning their inconstancy are worthy of further investigation. After the partial failure of these two attempts, the nitrates were resorted to with the satisfactory and interesting results described above.

These measurements were carried on in the Laboratory of Physical Chemistry in Boylston Hall, Harvard University. I wish to thank Professor Theodore W. Richards for his kindly interest and aid in the investigation, and especially for his many helpful suggestions when experimental difficulties were encountered.